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FLUX PINNING AND CRITICAL CURRENTS IN A-15 SUPERCONDUCTORS

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by

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The relationship between processing, microstructure, and properties was studied for A-15 compounds in multifilamentary composites produced by solid-state diffusion and in thin-film samples produced by vapor deposition. Grain sizes of A-15 superconducting compounds were measured by transmission electron microscopy of multifilamentary composites reacted at various temperatures. Critical current densities at 4.2 K and fields up to 6 T were found to be similar for niobium-tin, vanadium-gallium, and vanadium-silicon of the

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20. ABSTRACT (Cont'd)

same grain size. Study of the Cu-V-Si phase diagram led to the production of improved multifilamentary vanadium-silicon conductors. The effects of various alloying elements on A-15 layers produced by solid-state diffusion were studied. The most promising new observation was that tantalum can be incorporated into niobium-tin reaction layers, leading to an enhancement of critical currents at high fields. The critical temperature of vapor-deposited, niobium-germanium films has been studied as a function of deposition rates, flux stoichiometry, substrate temperature, and, especially, gas composition. Introduction of controlled levels of oxygen has been found to expand the range of Nb-Ge flux ratios which yield high critical temperatures.

GENERAL ELECTRIC

FLUX PINNING AND CRITICAL CURRENTS IN A-15 SUPERCONDUCTORS

by

J. D. Livingston and R. A. Sigsbee

INTRODUCTION

Two of the most significant superconducting materials developments of recent years have been the development of multifilamentary composites based on V_3Ga and Nb_3Sn and the production of metastable Nb_3Ge films displaying superconductivity up to 23 K. Although these advances have intensified the interest and research activity on A-15 compounds, much remains unknown about the fundamental relationships between processing variables, metallurgical microstructure, and superconducting properties of these materials.

On January 1, 1975, this program was undertaken by General Electric Corporate Research and Development to improve the understanding in this area, specifically in multifilamentary composites produced by solid-state diffusion techniques and in thin-film samples produced by vapor deposition. The program is focused toward development of sound processing-structure-properties relationships for various binary A-15 compounds, and toward determination of the effects of various ternary alloying elements on microstructure and properties.

AFOSR-supported work on processing and properties has been closely integrated with General Electric-supported work on microstructures. Because these programs are so intimately related, this report will describe the results of both programs.

RESEARCH OBJECTIVES

1. Grain Size Studies

Determine and compare the relationships between reaction temperature, grain size, and critical current densities for multifilamentary Nb_3Sn, V_3Ga, and V_3Si.

2. Alloying Studies

Determine the effects of various alloying elements on the processing, structure, and properties of multifilamentary A-15 composites.

3. Ternary Studies

Examine the effects of heat treatment of ternary A-15 compounds in an attempt to produce precipitation and improved superconducting properties.

4. Thin-Film Studies

Generate the critical deposition parameter surface for the Nb/Ge ratio, oxygen pressure, and substrate temperature for PVD Nb_3Ge films, and post-deposition heat-treatment behavior. Determine the mechanism for oxygen stabilization of Nb_3Ge.

RESEARCH ACCOMPLISHMENTS

1. Grain Size Studies

Commercial multifilamentary Nb_3Sn or V_3Ga superconducting composites are made by the bronze technique, i.e., by reaction between Nb and Cu(Sn) or between V and Cu(Ga). Earlier work had shown that grain size was the most important microstructural parameter in determining critical currents in such conductors. However, earlier results by different investigators using different techniques were inconsistent, and, in particular, indicated large and unexplained differences between Nb_3Sn and V_3Ga. Similar data had not been gathered for V_3Si because in conductors studied earlier by investigators, the bronze technique produced mostly V_5Si_3 and only a small proportion of V_3Si.

Composition-variation studies were made to determine the relevant portion of the Cu-V-Si phase diagram (Figure 1). Using these results, proper

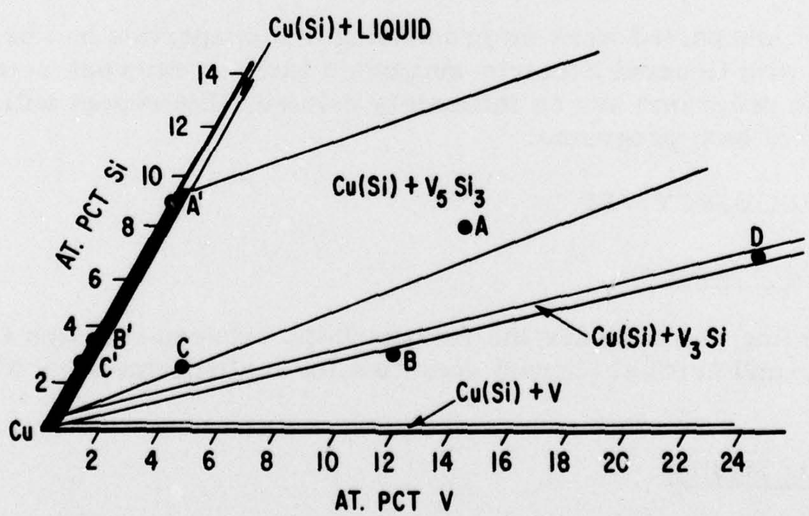

Figure 1. Schematic Representation of Cu-Rich Corner of the Cu-V-Si Phase Diagram as Determined from These Experiments. Points A', B', and C' represent average matrix concentrations of the various conductors studied. Points A, B, C, and D represent overall conductor concentrations. A conductor represented by D, with a matrix composition of A', will form predominantly V_5Si_3 initially, but will eventually contain mostly V_3Si.

control of Si concentration and the V/Si ratio led to the production of a multifilamentary composite in which, for the first time, V_3Si was produced without a substantial proportion of V_5Si_3.

These results were also important in focusing attention on the importance of ternary phase diagrams in the production of A-15 compounds by the bronze process. Consideration of evidence in the literature on the Cu-Nb-Al, Cu-Nb-Ga, and Cu-Nb-Ge phase diagrams led to the conclusion that Nb_3Al, Nb_3Ga, and Nb_3Ge cannot be satisfactorily produced by the bronze technique.

Multifilamentary composites of Nb_3Sn, V_3Ga, and V_3Si were produced using identical geometries and processing techniques. Grain sizes were measured for all three compounds by transmission electron microscopy, and correlated with superconducting critical-current measurements (Figures 2 and 3). Grain sizes of V_3Ga were found to be larger than those of Nb_3Sn and V_3Si formed at the same temperature, but much smaller than those reported by earlier workers. Critical current densities at 4.2 K and fields up to 6 T were similar for V_3Ga, Nb_3Sn, and V_3Si of the same grain size.

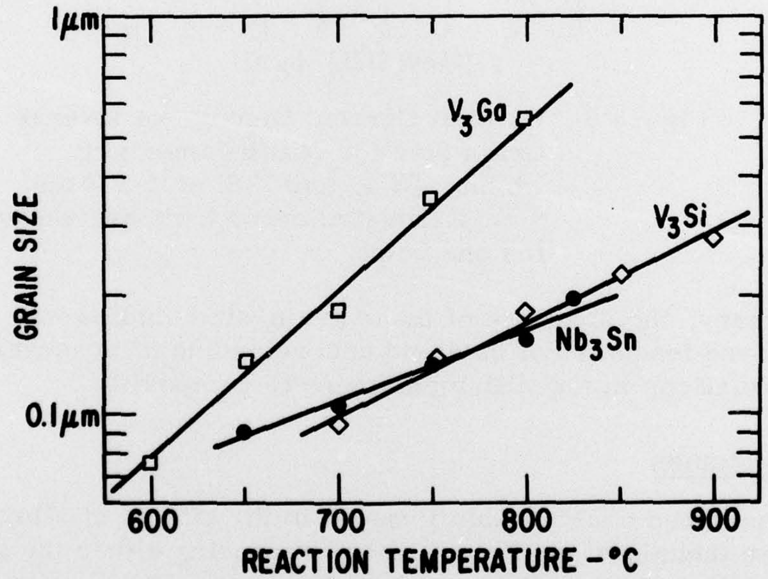

Figure 2. Average Grain Size (determined by transmission electron microscopy) as a Function of Reaction Temperature for Multifilamentary Nb_3Sn, V_3Ga, and V_3Si.

As necessary background for these grain-size studies and the alloying studies to be reported below, considerable data were gathered on the growth kinetics and chemical compositions of various A-15 reaction layers. Microprobe measurements indicated that the copper contents of the A-15 layers were low, in contrast to some reports in the literature.

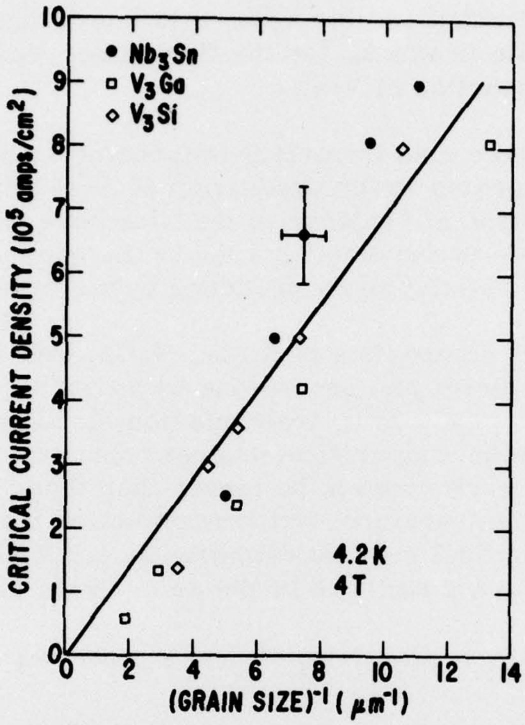

Figure 3. Critical Current Density vs Inverse Grain Size for Multifilamentary Nb_3Sn, V_3Ga, and V_3Si at 4.2 K and 4 T. Estimated error bars are shown for one point.

In summary, the objective of these grain-size studies was met, providing improved fundamental data and understanding of processing-structure-properties relations in multifilamentary A-15 composites.

2. Alloying Studies

There has been considerable interest in the effects of alloying elements on the bronze technique, with the hope of improving either the growth kinetics or the critical temperature, critical field, or critical currents of the A-15 compounds produced. Alloying elements can be introduced either into copper-rich matrix, into the refractory-metal filaments, or applied as an external coating. Each of these approaches was examined in this program and various alloying elements were studied.

Microprobe studies showed that, in general, alloying elements introduced into the matrix or applied to the composite externally did not enter the A-15 reaction layer to a significant degree. An exception was Ga, which was incorporated in Nb_3Sn to the level of a few percent, producing an improvement in superconducting properties. Additions of Al to the matrix, or added as an external coating, were not incorporated appreciably into Nb_3Sn, but did produce a slight improvement of growth kinetics at 600°C and 700°C. During the course of this contract, these results were also reported by other workers.

Most of the alloying elements studied have been those, like Ga and Al, expected to substitute on the B lattice sites of the A_3B compounds. Alloying elements such as Ta, expected to substitute on the A lattice sites, had not been studied by previous workers. Various Nb(Ta) alloys were prepared and reacted with a Cu(Sn) matrix. Microprobe studies showed that tantalum was fully incorporated into the A-15 reaction layers. The most concentrated alloy produced a reaction layer of composition approximately Nb_2TaSn, by far the most concentrated ternary A-15 compound yet produced by the bronze technique. Superconducting measurements indicated that concentrations of Ta of approximately 5 at. percent produce improvements in the high-field critical currents of Nb_3Sn (Figure 4). Substantially higher Ta concentrations lead to decreased critical temperatures and decreased growth kinetics.

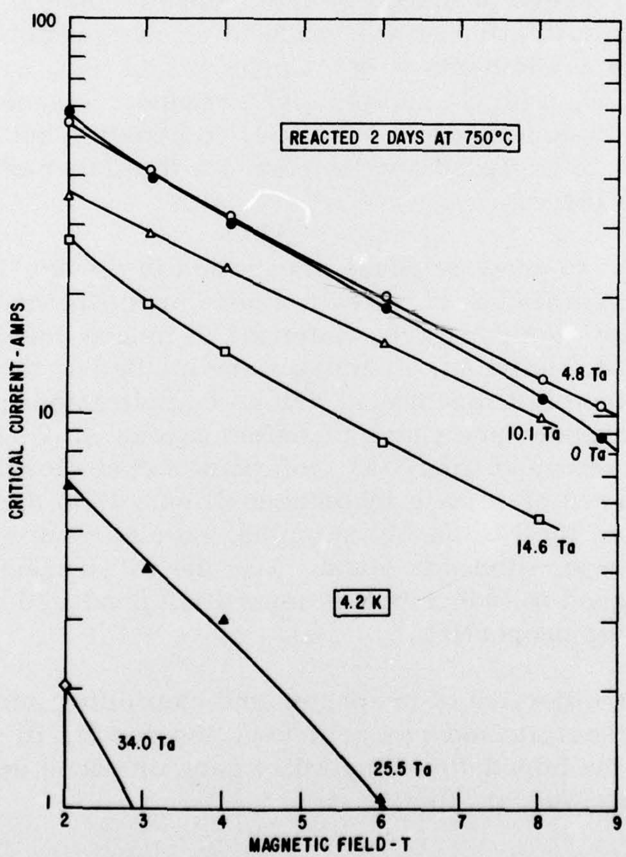

Figure 4. Critical Current vs Applied Field at 4.2 K for Various Monofilamentary Conductors with Nb(Ta) Cores in Cu(Sn) Matrices, Heated for 2 Days at 750°C. At high fields, the conductor containing 4.8 at. percent Ta had higher critical currents than that without Ta. At longer reaction times, this enhancement is greater.

The general objectives of this portion of the program were met, and several alloying elements were identified of possible technological promise.

3. Ternary Studies

Mutual solid solubility exists between many A-15 compounds, allowing the production of ternary compounds of the form $(A, A')_3B$ or $A_3(B, B')$. It seemed worthwhile to explore the possibility that in some of these systems a low-temperature miscibility gap might exist, allowing the production of fine-scale phase separation or precipitation by appropriate heat treatment. Such precipitation would be expected to lead to increased flux pinning and enhanced critical currents.

The systems chosen for study were $Nb_3(Sn, Al)$, $Nb_3(Sn, Sb)$, $V_3(Ga, Si)$, $(Nb, V)_3$ Ga, $(V, Mn)_3Si$, and $(Nb, Ta)_3Sn$. The first five were studied in the form of arc castings of various compositions. The last was studied in the form of reaction layers produced by the bronze technique as described in the previous section. An attempt was made to produce reaction layers of V_3(Ga, Si) by reaction of V filaments with a Cu(Ga, Si) matrix, but reaction produced only V_5Si_3 and V_3Si, with Ga completely excluded. A second attempt was made by applying thin Si coatings to a V-Cu(Ga) composite, but here mostly V_3Ga formed, with the Si excluded and limited to a thin layer of vanadium silicide outside the V_3Ga layer.

In an attempt to produce phase separation in the arc-cast samples, alloys were first annealed at elevated temperatures (intended to homogenize) and then at much lower temperatures (intended to induce precipitation). After each stage of heat treatment, samples were studied by x-ray diffraction and optical and electron microscopy. Various complications were encountered, including high-temperature phase transformations (in V-Ga-Si and Nb-Sn-Al), a new ordered compound (Nb_2VGa), volatilization at elevated temperatures, and various degrees of sample inhomogeneities. With the exception of a small volume fraction of the $Nb_3(Sn, Sb)$ samples, no clear-cut evidence of precipitation or phase separation was found. For the $(Nb, Ta)_3Sn$ composites, heat treatments designed to induce phase separation produced no significant change in superconducting properties.

Although the objective of preparing and examining numerous ternary A-15 compounds for precipitation was achieved, the results in most cases revealed no evidence for the hoped-for miscibility gaps or phase separation. The Nb-Sn-Sb system may warrant further study.

4. Thin-Film Studies

This effort has concentrated on the growth of Nb_3Ge films by physical vapor deposition (PVD), with the overall goal of determining the effects of the various processing parameters on critical temperature. The variation of PVD film properties as a function of deposition rates, Nb/Ge flux geometry, substrate temperature, and gas composition was studied. At the beginning of this program, reports in the literature indicated very clean vacuum conditions and high-purity films were necessary to obtain optimum critical temperatures of Nb_3Ge. A major result of the present work has been to show instead that active residual gas present in the deposition system has a significant effect on the T_c and relative phase stability of Nb_3Ge during film growth.

Controlled levels of O_2 have been introduced during film growth at nominal substrate temperatures (T_S) ranging from 900° to 1050°C. This has been found to open a "window" of allowed Nb/Ge impingement flux ratios which yield good T_c's. For example with O_2 present, a T_S of 1000°C, and a total deposition rate of 6Å/sec, the Nb/Ge flux ratio can vary from 1.8 to 2.4 and still produce T_c onsets well above 21 K. The T_c widths are less than 0.7 K when the O_2 level is from 3 to 5 x 10^{-7}mm Hg. Higher O_2 pressures can degrade the resulting film properties and at excessive levels yield mixtures of Nb_3Ge and NbO. The dependence of film T_c's upon Nb/Ge flux ratio is much more critical without O_2, and high T_c occurs within a narrow flux ratio.

Measurement of the critical processing parameters at 950° and 900°C was completed, and some data at 1050°C were also obtained. The results are similar in most respects to those found at a T_S of 1000°C. At 900°C, however, the Nb/Ge flux ratio and O_2 level are much more critical if T_c's above 20 K are to be obtained. Excess Ge is present in the optimum Nb/Ge flux ratio at all temperatures investigated. The optimum shifts from 2.3 at 1000°C to 2.5 at 900°C for films grown without O_2. All of the films with good T_c's have been grown under conditions in which the Ge flux is in excess of the ideal ratio of 3/1 for Nb/Ge. These various results are summarized in Figures 5, 6, and 7.

The data mentioned above indicate that desorption of excess Ge is occurring during Nb_3Ge film growth. Data of T_c vs the Nb/Ge ratio show an O_2 enhancement of T_c in 2 flux regimes: Nb/Ge>2.3 and Nb/Ge<2.3. It is postulated that for Nb/Ge > 2.3 the O_2 stabilizes the A-15 phase with a higher than equilibrium Ge content, reducing the Ge desorption rate during film growth. With no O_2 present, as the Ge flux is increased (Nb/Ge decreasing toward 2.3) metastable A-15 material with increasing Ge content is grown and the T_c increases. With still higher Ge rates, nucleation of the $\sigma(Nb_5Ge_3)$ phase occurs and the film structure is a mixture of A-15 and σ phases. This σ phase can act as a competing sink for Ge adatoms and lower the Ge content and T_c of the contiguous A-15 phase. X-ray diffraction data indicate the presence of σ phase when Nb/Ge is $\leq$ 1.9 if O_2 is not admitted during growth. These films also have lower T_c's. With controlled O_2 levels the σ phase is not found. The T_c enhancement of films grown with O_2 and excess Ge flux are thought to be the result of several concurrent effects:

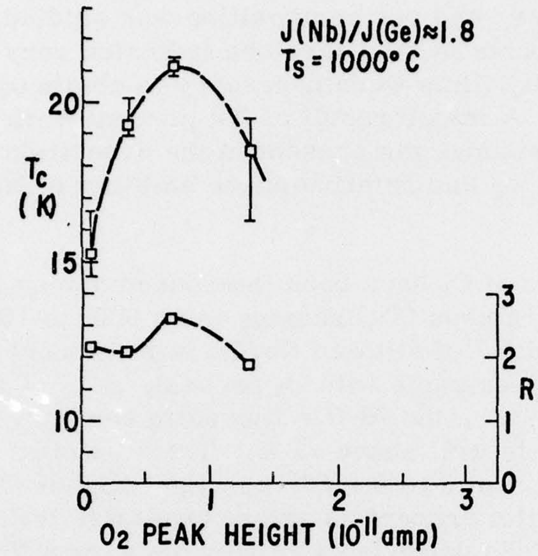

Figure 5. Critical Temperature of Nb_3Ge PVD Films vs Oxygen Concentration in the Chamber Atmosphere (as measured by mass spectrometry) for a Particular Nb/Ge Flux Ratio

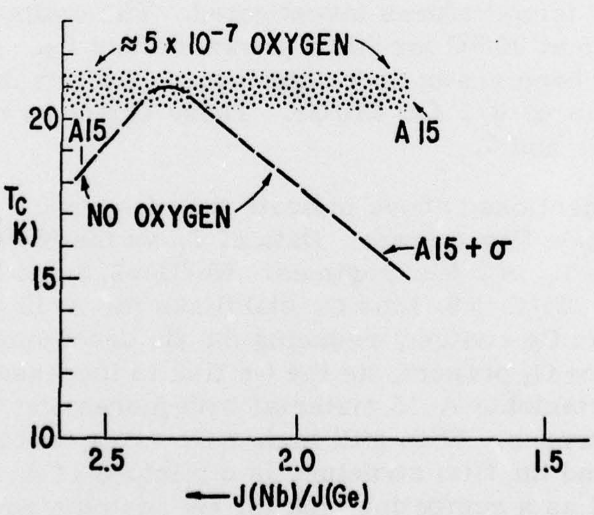

Figure 6. Critical Temperature of Nb_3Ge PVD Films vs Nb/Ge Flux Ratio With and Without Oxygen. The presence of the oxygen greatly widens the range of flux ratios that yield critical temperatures.

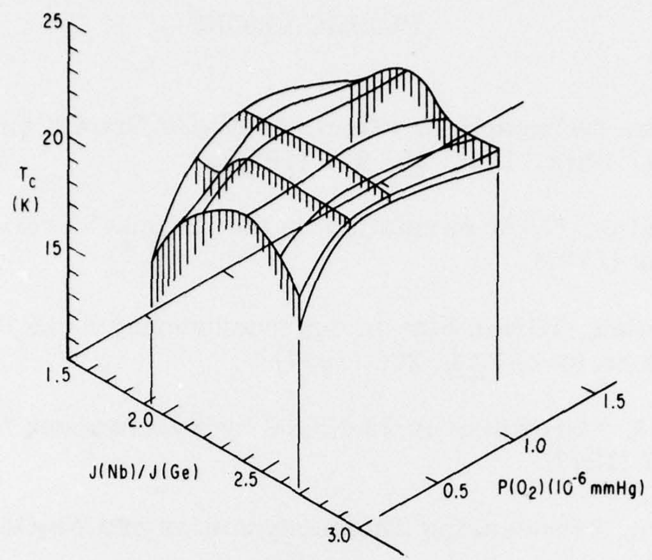

Figure 7. Three-Dimensional Surface Constructed by Accumulating Data, Such as in Figures 5 and 6 for Nb_3Ge Films Deposited on a 1000°C Substrate.

- O_2 stabilization of Ge-rich A-15 phase
- Enhanced desorption of excess Ge, possibly via the formation of volatile GeO
- O_2 reduction of the stability of Nb_5Ge_3

Experimental and theoretical work has enabled us to thermodynamically model the deposition process and elucidate the important factors.

The effects of annealing at 725°C on films with initial T_c's of ~21 K were found to be detrimental. T_c onset reductions from 0. 6 to 0. 9 K were observed and T_c widths broadened, with an accompanying reduction in resistivity ratios. Annealing of high T_c films at 625°C caused a similar reduction of T_c's and resistivity ratios and an increase in T_c transition widths.

The primary objectives of the thin-film portion of the program were met. However, detailed quantification and interpretation of the effects of processing parameters, expecially oxygen pressure, on Nb_3Ge films, required so much effort that other initial objectives (e.g., PVD of Nb_3Si) could not be accomplished.

PUBLICATIONS

1. R. A. Sigsbee, "Atmosphere Effects on Nb_3Ge Growth and Superconductivity," Appl. Phys. Lett. 29, 211 (1976).

2. J. D. Livingston, "V_3Si Formation by the 'Bronze' Process," J. Mater. Sci. 12, 1759 (1977).

3. J. D. Livingston, "Grain Size in Superconducting A-15 Reaction Layers," Phys. Status Solidi (A) 44, 295 (1977).

4. R. A. Sigsbee, "Growth of A-15 Nb_3Ge by Evaporation," Trans. IEEE Mag-13, 307 (1977).

5. R. A. Sigsbee, "Processing Thermodynamics and Nb_3Ge Growth" (in preparation).

6. J. D. Livingston, "Effect of Ta Additions on Bronze-Processed Nb_3Sn" (in preparation).

7. J. D. Livingston, "A-15 Compound Formation by the Bronze Process" (invited review paper, in preparation).

PRESENTATIONS AND INTERACTIONS

1. R.A. Sigsbee, "Growth of A-15 Nb_3Ge by Evaporation," Applied Superconductivity Conference, Stanford University, August 1976.

2. R.A. Sigsbee, "Impurity Stabilization of Nb_3Ge," AIME Symposium on Superconducting Materials and Applications, Niagara Falls, September 1976.

3. J.D. Livingston, "Multifilamentary A-15 Composites," AIME Symposium on Superconducting Materials and Applications, Niagara Falls, September 1976.

4. J.D. Livingston, "V_3Si Formation by the 'Bronze' Process," AIME Annual Meeting, Atlanta, March 1977.

5. R.A. Sigsbee, "Oxygen Effects on High T_cNb_3Ge," AIME Symposium on Metallurgy of Superconducting Materials, Chicago, October 1977.

6. J.D. Livingston, "Grain Size in A-15 Reaction Layers," AIME Symposium on Metallurgy of Superconducting Materials, Chicago, October 1977.

7. J.D. Livingston, "Superconducting A-15 Filamentary Conductors," Annual Meeting of German Metallurgical Society, to be held in Innsbruck, Austria, May 1978.

8. J.D. Livingston, "Effect of Ta Additions on Bronze-Processed Nb_3Sn," Intermag Conference, to be held in Florence, Italy, May 1978.

In addition to the numerous interactions with other workers in superconductivity at the above symposia, close contact has been maintained with workers at Intermagnetics General Corporation and General Electric Company concerning their work on the Wright-Patterson Air Force Base Manufacturing Technology Program for the work on the development of a Nb_3Sn multifilamentary conductor for an airborne superconducting generator. These workers have included J. Hughes and D. L. Martin of General Electric and A. Petrovich, M. Walker and B. Zeitlin of IGC. Information concerning conductor processing, heat treatment, microstructure, properties, and measurement techniques has been exchanged. Contact has also been maintained with D. Dew-Hughes and M. Suenaga of Brookhaven National Laboratory, R.H. Hammond of Stanford University, K. Tachikawa and K. Yasukochi of Japan, U. Zwicker and H. Hillmann of Germany, and other workers active in the study of multifilamentary and thin-film A-15 superconductors.

PATENTS

The following three patent applications were filed for R. A. Sigsbee on July 18, 1977.

RD-9053 - Nb_3Ge Superconductive Films
RD-10155 - Nb_3Ge Superconductive Films Grown in Air
RD-10156 - Nb_3Ge Superconductive Films Grown in Nitrogen

To comply with the Examiner's request for restriction between process and product, three additional cases will be filed shortly for R. A. Sigsbee, and these are:

RD-10619 (Div. of RD-9053)
RD-10620 (Div. of RD-10155)
RD-10621 (Div. of RD-10156)

The following patent dockets were opened for J. D. Livingston:

RD-8894 - Precipitation-Hardened Multifilamentary A-15 Superconductors
RD-8895 - V_3Si Superconducting Composites
RD-10216 - $(Nb, Ta)_3Sn$ Superconducting Composites

To date, patent applications have not been filed for these dockets.

PERSONNEL

Dr. James D. Livingston - Physicist

EDUCATION: Bachelor of Engineering Physics, Cornell University, 1952; MS in Engineering and Applied Physics, Harvard University, 1953; PhD in Engineering and Applied Physics, Harvard University, 1956.

EXPERIENCE: Since 1956, Dr. Livingston has been employed at the General Electric Research and Development Center. His research has dealt with the relation between metallurgical microstructure and the superconducting, ferromagnetic, and mechanical properties of metals and alloys. He is author or coauthor of over 60 publications.

In superconductivity, his research has primarily been concerned with flux pinning in type II superconductors. His 20 publications in this field treat flux pinning by dislocations, normal and superconducting precipitates, ferromagnetic particles, martensitic transformation, eutectic structures, etc. As a result of this body of work, he was invited by the Canadian Society of Metal Physics to present their 1971 MacDonald Memorial Lecture on the subject of "Superconductivity and Superconducting Materials." His comprehensive monograph on "The Effects of Metallurgical Variables on Superconducting Properties," written with H. W. Schadler, has been a standard reference work in this field since 1964.

Dr. Raymond A. Sigsbee - Metallurgist

EDUCATION: Journeyman Diemaker, Ford Motor Co., 1956; BS in Mechanical Engineering, University of Michigan, 1960; MS in Metallurgical Engineering, University of Michigan, 1961; PhD in Metallurgy, Carnegie-Mellon Institute, 1966.

EXPERIENCE: In his research at Carnegie, Dr. Sigsbee studied the nucleation and growth of alloy and compound thin films formed by physical vapor deposition methods. This work led to extensive experimental and theoretical insights into the problems of multicomponent film growth.

Since joining General Electric in 1966, his work has primarily focused on materials for electronic applications. This has involved applied and basic studies of thin film problems in nucleation and growth, interdiffusion and stability in multilayer structures and semiconductor contact materials. A study of the direct-current electromigration failure mechanism of conductors in solid-state devices was completed recently. His efforts were also concerned with radiation damage in insulators and the thermo-mechanical response of composite materials to pulsed radiation. He is author or coauthor of 11 publications in these areas, was an invited lecturer on "Heterogeneous Nucleation" at the 1971 Gordon Conference on Crystal Growth, and is joint American editor of Electrocomponent Science and Technology.